

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 600 586 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
10.12.1997 Bulletin 1997/50

(51) Int Cl.⁶: **G03C 1/498**

(21) Application number: **93307739.8**

(22) Date of filing: **29.09.1993**

(54) Photothermographic elements

Photothermographische Elemente

Éléments photothermographiques

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **30.11.1992 US 983125**

(43) Date of publication of application:
08.06.1994 Bulletin 1994/23

(73) Proprietor: **MINNESOTA MINING AND
MANUFACTURING COMPANY**
St. Paul, Minnesota 55133-3427 (US)

(72) Inventors:
• **Phillip, James B., c/o Minnesota Mining and
St. Paul, Minnesota 55133-3427 (US)**

• **Skoug, Paul G., c/o Minnesota Mining and
St. Paul, Minnesota 55133-3427 (US)**

(74) Representative: **Bowman, Paul Alan et al
LLOYD WISE, TREGEAR & CO.,
Commonwealth House,
1-19 New Oxford Street
London WC1A 1LW (GB)**

(56) References cited:
EP-A- 0 223 606 US-A- 4 281 060

• **PATENT ABSTRACTS OF JAPAN vol. 12, no. 266
(P-735) (3113) 26 July 1988 & JP-A-63 052 137
(KONICA) 5 March 1988**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 600 586 B1

Description

The invention relates to a photothermographic silver halide material and method for producing in such a material improved fog stability on shelf aging by a combination of an isocyanate and a halogenated compound.

Silver halide photothermographic imaging materials, often referred to as "dry silver" compositions because no liquid development is necessary to produce the final image, have been known in the art for many years. These imaging materials basically comprise a light insensitive, reducible silver source, a light sensitive material which generates silver when irradiated, and a reducing agent for the silver source. The light sensitive material is generally photographic silver halide which must be in catalytic proximity to the light insensitive silver source. Catalytic proximity is an intimate physical association of these two materials so that when silver specks or nuclei are generated by the irradiation or light exposure of the photographic silver halide, those nuclei are able to catalyze the reduction of the silver source by the reducing agent. It has been long understood that silver is a catalyst for the reduction of silver ions and the silver-generating light sensitive silver halide catalyst progenitor may be placed into catalytic proximity with the silver source in a number of different fashions, such as partial metathesis of the silver source with a halogen-containing source (e.g., U.S. Pat. No. 3,457,075), coprecipitation of the silver halide and silver source material (e.g., U.S. Pat. No. 3,839,049), and any other method which intimately associates the silver halide and the silver source.

Photothermographic emulsions, in a manner similar to photographic emulsions and other light sensitive systems, tend to suffer from fog. Fog is spurious image density which appears in unexposed areas of the element and is often reported in sensitometric results as D_{min} . Traditionally, photothermographic materials have suffered from fog instability on shelf aging. The fog level rises steadily as the materials reach extended age such as one year at room temperature (ambient conditions). Adding to the difficulty of fog control on shelf aging is the fact that the developer is incorporated in the photothermographic element which is not the case in most silver halide photographic systems. The need for shelf life extenders in photothermographic elements is therefore considered to be very important. The fog level of freshly prepared photothermographic materials will be referred to as initial fog. A great deal of effort has been directed towards minimizing the initial fog and stabilizing the fog level on shelf aging. Mercuric salts are described as antifoggants in U.S. Patent No. 3,589,903. Fog reduction has been described for organic carboxylic acids such as benzoic and phthalic acids in U.S. Patent No. 4,152,160, for benzoyl benzoic acid compounds in U.S. Patent No. 4,784,939, for indane or tetralin carboxylic acids in U.S. Patent No. 4,569,906, for dicarboxylic acids in U.S. Patent No. 4,820,617 and for heteroaromatic carboxylic acids in U.S. Patent No. 4,626,500. Halogenated compounds have also been shown to be strong antifoggants and are described in U.S. Patents 4,546,075, 4,756,999, 4,452,885, 3,874,946 and 3,955,982. Halogen molecules or halogen molecules associated with a heteroatom ring are also useful antifoggants and are described in U.S. Patent No. 5,028,523. However, these compounds individually or in combination were not found to produce sufficient fog stability on shelf aging of the photothermographic element.

Diisocyanates have been used to improve the physical properties of photothermographic materials. They will crosslink the resin or binder which toughens the layer and reduces or eliminates scratching during hot roll processing. Crosslinking by diisocyanates is described in U.S. Patent No. 4,281,060 and in combination with boric acid in U.S. Patent No. 4,558,003. These patents used diisocyanates to harden or crosslink the resin.

According to the present invention there is provided a photothermographic emulsion comprising in one or two layers a silver salt of an organic acid, silver halide, a reducing agent for silver ion, and a binder, the silver salt of an organic acid and the silver halide being present in one layer, characterised in that the emulsion contains, as an antifoggant, the combination of 1) at least one compound having an isocyanate group, and 2) a halogenated antifoggant compound which has an aromatic or heteroaromatic group having at least one perhalogenated alkyl group thereon.

It has been found the generation of fog, in particular on shelf aging, in photothermographic elements comprising photosensitive silver halide, organic silver salt oxidizing agent and reducing agent for silver ion can be reduced by the combination of an isocyanate and the recited halogenated compound.

In the emulsions of the invention the ability of the isocyanate to harden or crosslink is not critical to whether the isocyanate will act as a fog stabilizer on shelf aging. Octadecyl isocyanate, which has only a single isocyanate group, cannot crosslink the resin but still improves the fog stability on shelf aging.

Suitable isocyanate compounds are those of the formula (I):



in which:

v represents 0, 1, or 2,

L represents a linking group which can be an alkyl, alkene, aryl or a mixed alkylaryl group, or when v = 0, L

represents a terminating group.

The aryl ring may also carry substituents with examples of preferred substituents being selected from the class consisting of halogen (e.g. Br and Cl), hydroxy, amino, carboxy and alkoxy.

Specific examples of isocyanate compounds along with the manufacturer and class are set forth below. The examples include aliphatic, aromatic and polymeric isocyanates.

- IC-1 Desmodur N100, Mobay, aliphatic isocyanate
- IC-2 Desmodur N3300, Mobay, aliphatic isocyanate
- IC-3 Mondur TD-80, Mobay, aromatic isocyanate
- IC-4 Mondur M, Mobay, aromatic isocyanate
- IC-5 Mondur MRS, Mobay, polymeric isocyanate
- IC-6 Desmodur W, Mobay, aliphatic isocyanate
- IC-7 Papi 27, Dow, polymeric isocyanate
- IC-8 Isocyanate T 1890, Huels, aliphatic isocyanate
- IC-9 Octadecyl Isocyanate, Aldrich, aliphatic isocyanate

The isocyanates are used in general amount of at least 0.0002 moles/mole of silver. Usually the range is between 0.002 and 2 moles of the compound per mole of silver and preferably between 0.003 and 0.3 moles of compound per mole of silver.

Isocyanates improve the fog stability on shelf aging of photothermographic systems incorporating a halogenated antifoggant compound. The antifoggant preferably has at least one brominated alkyl group thereon, more preferably at least one tribromomethane group which may be directly attached to the aromatic or heteroaromatic group or bonded through a linking group, e.g. sulphonyl.

The preferred antifoggant compounds are represented by the formula:



in which:

y represents 0 or 1,

X represents a halogen atom, and

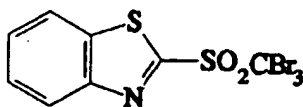
Ar represents an aromatic or heteroaromatic group.

A detailed listing of compounds included in formula II is contained in U.S. Patent Nos. 4,546,075, 4,756,999, 4,452,885, 3,874,946 and 3,955,982.

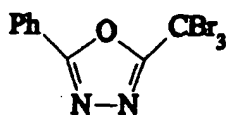
Where the term group is used in describing substituents, substitution is anticipated on the substituent for example, alkyl group includes for example ether groups (e.g., $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-}$), haloalkyls, nitroalkyls, carboxyalkyls, hydroxyalkyls, sulfoalkyls while the term alkyl includes only hydrocarbons. Substituents which react with active ingredients, such as very strongly electrophilic or oxidizing substituents, would of course be excluded as not being inert or harmless.

The halogenated compounds used in the present invention are generally incorporated in the silver or topcoat layer in a content of 5×10^{-4} mole to 0.5 mole preferably 5×10^{-3} to 5×10^{-2} mole, per mole of total silver.

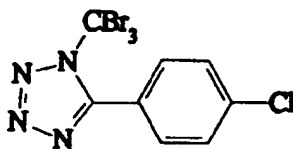
Specific examples of the halogenated antifoggant compounds used in the present invention are listed below.



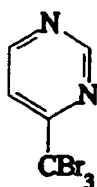
AF-1



AF-2



AF-3



AF-4

The photothermographic dry silver emulsions of this invention may be constructed of one or more layers on a substrate. Single layer constructions must contain the silver source material, the silver halide, the developer and binder as well as optional additional materials such as toners, coating aids, and other adjuvants. Two-layer constructions must contain the silver source and silver halide in one emulsion layer (usually the layer adjacent to the substrate) and some of the other ingredients in the second layer or both layers, although two layer constructions comprising a single emulsion layer containing all the ingredients and a protective topcoat are envisioned. Multicolor photothermographic dry silver constructions may contain sets of these bilayers for each color, or they may contain all ingredients within a single layer as described in U.S. Pat. No. 4,708,928. In the case of multilayer multicolor photothermographic articles the various emulsion layers are generally maintained distinct from each other by the use of functional or non-functional barrier layers between the various photosensitive layers as described in U.S. Pat. No. 4,460,681.

While not necessary for practice of the present invention, it may be advantageous to add mercury (II) salts to the emulsion layer(s) as an antifoggant. Preferred mercury (II) salts for this purpose are mercuric acetate and mercuric bromide.

The light sensitive silver halide used in the present invention may typically be employed in a range of 0.75 to 25 mol percent and, preferably, from 2 to 20 mol percent of organic silver salt.

The silver halide may be any photosensitive silver halide such as silver bromide, silver iodide, silver chloride, silver bromiodide, silver chlorobromiodide and silver chlorobromide. The silver halide may be in any form which is photosensitive including, but not limited to cubic, orthorhombic, tabular and tetrahedral, and may have epitaxial growth of crystals thereon.

The silver halide used in the present invention may be employed without modification. However, it may be chemically sensitized with a chemical sensitizing agent such as a compound containing sulfur, selenium or tellurium, or a compound containing gold, platinum, palladium, rhodium or iridium, a reducing agent such as a tin halide, or a combination thereof. The details of these procedures are described in T.N. James "The Theory of the Photographic Proc-

ess³, Fourth Edition, Chapter 5, pages 149 to 169.

The silver halide may be added to the emulsion layer in any fashion which places it in catalytic proximity to the silver source. Silver halide and the organic silver salt which are separately formed or "preformed" in a binder can be mixed prior to use to prepare a coating solution, but it is also effective to blend both of them in a ball mill for a long period of time. Further, it is effective to use a process which comprises adding a halogen-containing compound in the organic silver salt prepared to partially convert the silver of the organic silver salt to silver halide.

Methods of preparing these silver halide and organic silver salts and manners of blending them are known in the art and described in *Research Disclosure*, June 1978, item 17029, and U.S. Pat. No. 3,700,458.

The use of preformed silver halide emulsions of this invention can be unwashed or washed to remove soluble salts. In the latter case the soluble salts can be removed by chill-setting and leaching or the emulsion can be coagulation washed, e.g., by the procedures described in U.S. Pat. Nos. 2,618,556; 2,614,928; 2,565,418; 3,241,969; and 2,489,341. The silver halide grains may have any crystalline habit including, but not limited to cubic, tetrahedral, orthorhombic, tabular, laminar and platelet.

The organic silver salt may be any organic material which contains a reducible source of silver ions. Silver salts of organic acids, particularly long chain (10 to 30 preferably 15 to 28 carbon atoms) fatty carboxylic acids are preferred. Complexes of organic or inorganic silver salts wherein the ligand has a gross stability constant between 4.0 and 10.0 are also desirable. The silver source material should preferably constitute from about 5 to 30 percent by weight of the imaging layer.

The organic silver salt which can be used in the present invention is a silver salt which is comparatively stable to light, but forms a silver image when heated to 80°C or higher in the presence of an exposed photocatalyst (such as photographic silver halide) and a reducing agent.

Preferred organic silver salts include silver salts of organic compounds having a carboxy group. Non-limiting examples thereof include silver salts of an aliphatic carboxylic acid and a silver salt of an aromatic carboxylic acid. Preferred examples of the silver salts of aliphatic carboxylic acids include silver behenate, silver stearate, silver oleate, silver laurate, silver caproate, silver myristate, silver palmitate, silver maleate, silver fumarate, silver tartrate, silver linoleate, silver butyrate and silver camphorate and mixtures thereof. Silver salts with a halogen atom or a hydroxyl on the aliphatic carboxylic acid can also be effectively used. Preferred examples of the silver salts of aromatic carboxylic acids and other carboxyl group-containing compounds include silver benzoate, a silver substituted benzoate such as silver 3,5-dihydroxybenzoate, silver *o*-methylbenzoate, silver *m*-methylbenzoate, silver *p*-methylbenzoate, silver 2,4-dichlorobenzoate, silver acetamidobenzoate, silver *p*-phenyl benzoate, silver gallate, silver tannate, silver phthalate, silver terephthalate, silver salicylate, silver phenylacetate, silver pyromellitate, a silver salt of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione as described in U.S. Pat. No. 3,785,830, and silver salt of an aliphatic carboxylic acid containing a thioether group as described in U.S. Pat. No. 3,330,663.

Silver salts of compounds containing mercapto or thione groups and derivatives thereof can also be used. Preferred examples of these compounds include a silver salt of 3-mercapto-4-phenyl-1,2,4-triazole, a silver salt of 2-mercapto-benzimidazole, a silver salt of 2-mercapto-5-aminothiadiazole, a silver salt of 2-(ethylglycolamido)benzothiazole, a silver salt of thioglycolic acid such as a silver salt of an *S*-alkyl thioglycolic acid (wherein the alkyl group has from 12 to 22 carbon atoms), a silver salt of a dithiocarboxylic acid such as a silver salt of dithioacetic acid, a silver salt of a thioamide, a silver salt of 5-carboxylic-1-methyl-2-phenyl-4-thiopyridine, a silver salt of mercaptotriazine, a silver salt of 2-mercaptobenzoxazole, a silver salt as described in U.S. Pat. No. 4,123,274, for example, a silver salt of 1,2,4-mercaptotriazole derivative such as a silver salt of 3-amino-5-benzylthio-1,2,4-triazole, a silver salt of a thione compound such as a silver salt of 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione as disclosed in U.S. Pat. No. 3,301,678.

Furthermore, a silver salt of a compound containing an imino group may be used. Preferred examples of these compounds include silver salts of benzotriazole and derivatives thereof, for example, silver salts of benzotriazoles such as silver methylbenzotriazolate, silver salt of halogen-substituted benzotriazoles, such as silver 5-chlorobenzotriazolate, silver salts of carboimidobenzotriazole, silver salt of 1,2,4-triazoles or 1-*H*-tetrazoles as described in U.S. Pat. No. 4,220,709, silver salts of imidazoles and imidazole derivatives. Various silver acetylide compounds can also be used, for instance, as described in U.S. Pat. Nos. 4,761,361 and 4,775,613.

It is also found convenient to use silver half soaps, of which an equimolar blend of silver behenate and behenic acid, prepared by precipitation from aqueous solution of the sodium salt of commercial behenic acid and analyzing about 14.5 percent silver, represents a preferred example. Transparent sheet materials made on transparent film backing require a transparent coating and for this purpose the silver behenate full soap, containing not more than about four or five percent of free behenic acid and analyzing about 25.2 percent silver may be used.

The method used for making silver soap dispersions is well known in the art and is disclosed in *Research Disclosure*, April 1983, item 22812, *Research Disclosure*, October 1983, item 23419 and U.S. Pat. No. 3,985,565.

The light-sensitive silver halides may be advantageously spectrally sensitized with various known dyes including cyanine, merocyanine, styryl, hemicyanine, oxonol, hemioxonol and xanthene dyes. Useful cyanine dyes include those having a basic nucleus, such as a thiazoline nucleus, an oxazoline nucleus, a pyrroline nucleus, a pyridine nucleus,

an oxazole nucleus, a thiazole nucleus, a selenazole nucleus and an imidazole nucleus. Useful merocyanine dyes which are preferred include those having not only the above described basic nuclei but also acid nuclei, such as a thiohydantoin nucleus, a rhodanine nucleus, an oxazolidinedione nucleus, a thiazolidinedione nucleus, a barbituric acid nucleus, a thiazolinone nucleus, a malononitrile nucleus and a pyrazolone nucleus. In the above described cyanine and merocyanine dyes, those having imino groups or carboxyl groups are particularly effective. Practically, the sensitizing dyes to be used in the present invention may be properly selected from known dyes such as those described in U.S. Pat. Nos. 3,761,279, 3,719,495, and 3,877,943, British Pat. Nos. 1,466,201, 1,469,117 and 1,422,057, and can be located in the vicinity of the photocatalyst according to known methods. Spectral sensitizing dyes may be typically used in amounts of about 10^{-4} mol to about 1 mol per 1 mol of silver halide.

The reducing agent for the organic silver salt may be any material, preferably organic material, that can reduce silver ion to metallic silver. Conventional photographic developers such as phenidone, hydroquinones, and catechol are useful but hindered phenol reducing agents are preferred. The reducing agent should be present as 1 to 10 percent by weight of the imaging layer. In multilayer constructions, if the reducing agent is added to a layer other than an emulsion layer, slightly higher proportions, of from about 2 to 15 percent tend to be more desirable.

A wide range of reducing agents have been disclosed in dry silver systems including amidoximes such as phenylamidoxime, 2-thienylamidoxime and *p*-phenoxyphenylamidoxime, azines (e.g., 4-hydroxy-3,5-dimethoxybenzaldehydeazine); a combination of aliphatic carboxylic acid aryl hydrazides and ascorbic acid, such as 2,2'-bis(hydroxymethyl)propionyl- β -phenylhydrazide in combination with ascorbic acid; a combination of polyhydroxybenzene and hydroxylamine, a reductone and/or a hydrazine (e.g., a combination of hydroquinone and bis(ethoxyethyl)hydroxylamine, piperidinohexose reductone or formyl-4-methylphenylhydrazine); hydroxamic acids such as phenylhydroxamic acid, *p*-hydroxyphenylhydroxamic acid, and β -alaninehydroxamic acid; a combination of azines and sulfonamidophenols, (e.g., phenothiazine and 2,6-dichloro-4-benzenesulfonamidophenol); α -cyanophenylacetic acid derivatives such as ethyl- α -cyano-2-methylphenylacetate, ethyl α -cyanophenylacetate; bis- β -naphthols as illustrated by 2,2'-dihydroxy-1,1'-binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl, and bis(2-hydroxy-1-naphthyl)methane; a combination of bis- β -naphthol and a 1,3-dihydroxybenzene derivative, (e.g., 2,4-dihydroxybenzophenone or 2,4-dihydroxyacetophenone); 5-pyrazolones such as 3-methyl-1-phenyl-5-pyrazolone; reductones as illustrated by dimethylaminohexose reductone, anhydrodihydroaminohexose reductone, and anhydrodihydropiperidonehexose reductone; sulfonamido-phenol reducing agents such as 2,6-dichloro-4-benzenesulfonamidophenol, and *p*-benzenesulfonamidophenol; 2-phenylindane-1,3-dione; chromans such as 2,2-dimethyl-7-*t*-butyl-6-hydroxychroman; 1,4-dihydropyridines such as 2,6-dimethoxy-3,5-dicarboethoxy-1,4-dihydropyridine; bisphenols (e.g., bis(2-hydroxy-3-*t*-butyl-5-methylphenyl)methane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 4,4-ethylidene-bis(2-*t*-butyl-6-methylphenol), and 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane); ascorbic acid derivatives (e.g., 1-ascorbyl palmitate, ascorbyl stearate); and unsaturated aldehydes and ketones, such as benzil and biacetyl; 3-pyrazolidones and certain indane-1,3-diones.

In addition to the aforementioned ingredients, it may be advantageous to include additives known as "toners" that improve the image. Toner materials may be present, for example, in amounts from 0.1 to 10 percent by weight of all silver bearing components. Toners are well known materials in the photothermographic art as shown in U.S. Pat. Nos. 3,080,254; 3,847,612 and 4,123,282.

Examples of toners include phthalimide and *N*-hydroxyphthalimide; cyclic imides such as succinimide, pyrazoline-5-ones, and a quinazolinone, 3-phenyl-2-pyrazoline-5-one, 1-phenylurazole, quinazoline, and 2,4-thiazolidinedione; naphthalimides (e.g., *N*-hydroxy-1,8-naphthalimide); cobalt complexes (e.g., cobaltic hexammine trifluoroacetate); mercaptans as illustrated by 3-mercapto-1,2,4-triazole, 2,4-dimercaptopyrimidine, 3-mercapto-4,5-diphenyl-1,2,4-triazole and 2,5-dimercapto-1,3,4-thiadiazole; *N*-(aminomethyl)aryldicarboximides, (e.g., (*N*, *N*-dimethylaminomethyl)phthalimide, and *N*,*N*-(dimethylaminomethyl)naphthalene-2,3-dicarboximide); and a combination of blocked pyrazoles, isothiuronium derivatives and certain photobleaching agents (e.g., a combination of *N*,*N*-hexamethylene bis(1-carbamoyl-3,5-dimethylpyrazole), 1,8-(3,6-diazoctane)bis(isothiuronium trifluoroacetate) and 2-(tribromomethylsulfonyl)benzothiazole); and merocyanine dyes such as 3-ethyl-5[(3-ethyl-2-benzothiazolylidene)-1-methylethylidene]-2-thio-2,4-oxazolidinedione; phthalazinone and phthalazinone derivatives or metal salts or these derivatives such as 4-(1-naphthyl)phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone, and 2,3-dihydro-1,4-phthalazinedione; a combination of phthalazinone plus sulfinic acid derivatives (e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, and tetrachlorophthalic anhydride); quinazolidinediones, benzoxazine or naphthoxazine derivatives; rhodium complexes functioning not only as tone modifiers, but also as sources of halide ion for silver halide formation *in situ*, such as ammonium hexachlororhodate (III), rhodium bromide, rhodium nitrate and potassium hexachlororhodate (III); inorganic peroxides and persulfates (e.g., ammonium peroxydisulfate and hydrogen peroxide); benzoxazine-2,4-diones such as 1,3-benzoxazine-2,4-dione, 8-methyl-1,3-benzoxazine-2,4-dione, and 6-nitro-1,3-benzoxazine-2,4-dione; pyrimidines and asymmetric triazines (e.g., 2,4-dihydropyrimidine, 2-hydroxy-4-aminopyrimidine), azauracils, and tetrazapentalene derivatives (e.g., 3,6-dimercapto-1,4-diphenyl-1*H*,4*H*-2,3*a*,5,6*a*-tetrazapentalene, and 1,4-di(*o*-chlorophenyl)-3,6-dimercapto-1*H*,4*H*-2,3*a*,5,6*a*-tetrazapentalene).

A number of methods are known in the art for obtaining color images with dry silver systems including: a combination

of silver benzotriazole, well known magenta, yellow and cyan dye-forming couplers, aminophenol developing agents, a base release agent such as guanidinium trichloroacetate and silver bromide in poly(vinyl butyral) as described in U.S. Pat. Nos. 4,847,188 and 5,064,742; preformed dye release systems such as those described in U.S. Pat. No. 4,678,739; a combination of silver bromide, sulfonamidophenol reducing agent, silver behenate, poly(vinyl butyral), an amine such as *n*-octadecylamine and 2-equivalent or 4-equivalent cyan, magenta or yellow dye-forming couplers; leuco dye bases which oxidize to form a dye image (e.g., Malachite Green, Crystal Violet and para-rosaniline); a combination of *in situ* silver halide, silver behenate, 3-methyl-1-phenylpyrazolone and *N,N*-dimethyl-*p*-phenylenediamine hydrochloride; incorporating phenolic leuco dye reducing agents such as 2(3,5-di-(*t*-butyl)-4-hydroxyphenyl)-4,5-diphenylimidazole, and bis(3,5-di-(*t*-butyl)-4-hydroxyphenyl)phenylmethane, incorporating azomethine dyes or azo dye reducing agents; silver dye bleach processes (for example, an element comprising silver behenate, behenic acid, poly(vinyl butyral), poly(vinyl-butylal)peptized silver bromide emulsion, 2,6-dichloro-4-benzenesulfonamidophenol, 1,8-(3,6-diazaoctane)bis(isothiuronium-*p*-toluenesulfonate) and an azo dye can be exposed and heat processed to obtain a negative silver image with a uniform distribution of dye, and then laminated to an acid activator sheet comprising polyacrylic acid, thiourea and *p*-toluenesulfonic acid and heated to obtain well defined positive dye images); and amines such as aminoacetanilide (yellow dye-forming), 3,3'-dimethoxybenzidine (blue dye-forming) or sulfanilide (magenta dye forming) that react with the oxidized form of incorporated reducing agents such as 2,6-dichloro-4-benzenesulfonamidophenol to form dye images. Neutral dye images can be obtained by the addition of amines such as behenylamine and *p*-anisidine.

Leuco dye oxidation in such silver halide systems for color formation is disclosed in U.S. Pat. Nos. 4,021,240, 4,374,821, 4,460,681 and 4,883,747.

Silver halide emulsions containing the antifoggants used in this invention can be protected further against the additional production of fog and can be stabilized against loss of sensitivity during shelf storage. Suitable antifoggants, stabilizers, and stabilizer precursors which can be used alone or in combination, include thiazolium salts as described in U.S. Pat. Nos. 2,131,038 and 2,694,716; azaindenes as described in U.S. Pat. Nos. 2,886,437 and 2,444,605; mercury salts as described in U.S. Pat. No. 2,728,663; urazoles as described in U.S. Pat. No. 3,287,135; sulfocatechols as described in U.S. Pat. No. 3,235,652; oximes as described in British Pat. No. 623,448; nitrones; nitroindazoles; polyvalent metal salts as described in U.S. Pat. No. 2,839,405; thiuronium salts as described in U.S. Pat. No. 3,220,839; and palladium, platinum and gold salts described in U.S. Pat. Nos. 2,566,263 and 2,597,915; halogen-substituted organic compounds as described in U.S. Pat. Nos. 4,108,665 and 4,442,202; triazines as described in U.S. Pat. Nos. 4,128,557; 4,137,079; 4,138,265; and 4,459,350; and phosphorous compounds as described in U.S. Pat. No. 4,411,985.

Emulsions of the invention can contain plasticizers and lubricants such as polyalcohols (e.g., glycerin and diols of the type described in U.S. Pat. No. 2,960,404); fatty acids or esters such as those described in U.S. Pat. No. 2,588,765 and U.S. Pat. No. 3,121,060; and silicone resins such as those described in British Pat. No. 955,061.

The photothermographic elements used in the present invention may include image dye stabilizers. Such image dye stabilizers are illustrated by British Pat. No. 1,326,889; U.S. Pat. Nos. 3,432,300; 3,698,909; 3,574,627; 3,573,050; 3,764,337 and 4,042,394.

Photothermographic elements containing emulsion layers according to the present invention can be used in photographic elements which contain light absorbing materials and filter dyes such as those described in U.S. Pat. Nos. 3,253,921; 2,274,782; 2,527,583 and 2,956,879. If desired, the dyes can be mordanted, for example, as described in U.S. Pat. No. 3,282,699.

Photothermographic elements containing emulsion layers as described herein can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in U.S. Pat. No. 2,992,101 and U.S. Pat. No. 2,701,245.

Emulsions in accordance with this invention can be used in photothermographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts (e.g., chlorides or nitrates), evaporated metal layers, ionic polymers such as those described in U.S. Pat. Nos. 2,861,056 and 3,206,312 or insoluble inorganic salts such as those described in U.S. Pat. No. 3,428,451.

The binder may be selected from any of the well-known natural or synthetic resins such as gelatin, polyvinyl acetals, polyvinyl chloride, polyvinyl acetate, cellulose acetate, polyolefins, polyesters, polystyrene, polyacrylonitrile or polycarbonates. Copolymers and terpolymers are of course included in these definitions. The preferred photothermographic silver containing polymers are polyvinyl butyral, ethyl cellulose, methacrylate copolymers, maleic anhydride ester copolymers, polystyrene, and butadiene-styrene copolymers.

Optionally, these polymers may be used in combinations of two or more thereof. Such a polymer is used in an amount sufficient to carry the components dispersed therein, that is, within the effective range of the action as the binder. The effective range can be appropriately determined by one skilled in the art. As a guide in the case of carrying at least an organic silver salt, it can be said that a preferable ratio of the binder to the organic silver salt ranges from 15:1 to 1:2, and particularly from 8:1 to 1:1.

Photothermographic emulsions containing a stabilizer according to the present invention may be coated on a wide variety of supports. Typical supports include polyester film, subbed polyester film, poly(ethylene terephthalate) film, cellulose nitrate film, cellulose ester film, poly(vinyl acetate) film, polycarbonate film and related or resinous materials, as well as glass, paper or metal. Typically, a flexible support is employed, especially a paper support, which may be partially acetylated or coated with baryta and/or an α -olefin polymer, particularly a polymer of an α -olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like. Substrates may be transparent or opaque.

Substrates with a backside resistive heating layer may also be used in photothermographic imaging systems such as shown in U.S. Pat. Nos. 4,460,681 and 4,374,921.

Photothermographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in U.S. Pat. No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in U.S. Pat. No. 2,761,791 and British Pat. No. 837,095.

Additional layers may be incorporated into photothermographic articles of the present invention such as dye receptive layers for receiving a mobile dye image, an opacifying layer when reflection prints are desired, a protective topcoat layer and a primer layer as is known in the photothermographic art. Additionally, it may be desirable in some instances to coat different emulsion layers on both sides of a transparent substrate, especially when it is desirable to isolate the imaging chemistries of the different emulsion layers.

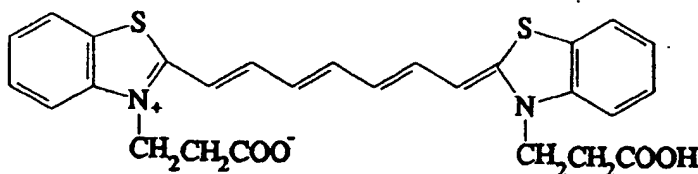
The present invention will be illustrated in detail in the following examples, but the embodiment of the present invention is not limited thereto. Examples A to H are comparative Examples.

Examples 1-27

A silver halide-silver behenate dry soap was prepared by the procedures described in U.S. Pat. No. 3,839,049. The silver halide totalled 9% of the total silver while silver behenate comprised 91% of the total silver. The silver halide was a 0.055 micron silver bromiodide emulsion with 2% iodide.

A photothermographic emulsion was prepared by homogenizing 300 g of the silver halide-silver behenate dry soap described above with 525 g toluene, 1675 g 2-butanone and 50 g poly(vinylbutyral) (B-76, Monsanto).

The homogenized photothermographic emulsion (500 g) and 100 g 2-butanone were cooled to 55°F (13°C) with stirring. Additional poly(vinylbutyral) (75.7 g B-76) was added and stirred for 20 minutes. Pyridinium hydrobromide perbromide (PHP, 0.45 g) was added and stirred for 2 hours. The addition of 3.25 ml of a calcium bromide solution (1 g of CaBr_2 and 10 ml of methanol) was followed by 30 minutes of stirring. The temperature was raised to 70°F (21°C) and the following were added in 15 minute increments with stirring: IR dye solution (8.8 mg D-1 dye in 7.1 g DMF), 4.2 g of supersensitizer solution (0.22 g 2-mercaptobenzimidazole, MBI, and 4 g methanol) and 16.6 of developer 1,1-bis (2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane.



D-1

The photothermographic emulsion was divided into 40 g portions. The control was coated at this stage without any additions. The remaining aliquots were treated with 3 levels of each isocyanate test compound added as 16% (w/w) solutions in 2-butanone. Table 1 contains the conversions from the amount of 16% isocyanate (IC) solution added per 40 g portion to actual grams of IC. Multiplying the grams of IC by the percent NCO content gives the NCO equivalents.

TABLE 1

Per 40 g Silver Portion					
Ex	IC	16% IC Solution (g)	grams IC	% NCO Content	NCO Equiv.
1	IC-1	0.125	0.020	0.220	0.0044
2	IC-1	0.250	0.040	0.220	0.0088
3	IC-1	0.500	0.080	0.220	0.0176
4	IC-2	0.126	0.020	0.216	0.0044
5	IC-2	0.253	0.041	0.216	0.0088
6	IC-2	0.506	0.081	0.216	0.0176
7	IC-3	0.056	0.009	0.480	0.0044
8	IC-3	0.112	0.018	0.480	0.0088
9	IC-3	0.225	0.036	0.480	0.0176
10	IC-4	0.084	0.013	0.330	0.0044
11	IC-4	0.169	0.027	0.330	0.0088
12	IC-4	0.338	0.054	0.330	0.0176

13	IC-5	0.088	0.014	0.320	0.0044
14	IC-5	0.175	0.028	0.320	0.0088
15	IC-5	0.350	0.056	0.320	0.0176
16	IC-6	0.088	0.014	0.320	0.0044
17	IC-6	0.175	0.028	0.320	0.0088
18	IC-6	0.350	0.056	0.320	0.0176
19	IC-7	0.089	0.014	0.314	0.0044
20	IC-7	0.175	0.028	0.314	0.0088
21	IC-7	0.350	0.056	0.314	0.0176
22	IC-8	0.153	0.024	0.180	0.0044
23	IC-8	0.306	0.049	0.180	0.0088
24	IC-8	0.612	0.098	0.180	0.0176
25	IC-9	0.190	0.031	0.142	0.0044
26	IC-9	0.380	0.062	0.142	0.0088
27	IC-9	0.770	0.124	0.142	0.0176

The photothermographic emulsion was coated on 3 mil (0.76×10^{-4} m) polyester base by means of a knife coater and dried at 175°F (80°C) for four minutes. The dry coating weight was 23 g/m².

An active, protective topcoat solution was prepared with the following ingredients:

256.0 g	acetone
123.0 g	2-butanone
50.0 g	methanol
20.2 g	cellulose acetate
2.89 g	phthalazine
1.55 g	4-methylphthalic acid
1.01 g	tetrachlorophthalic acid
0.90 g	tetrabromophthalic anhydride
1.50 g	tetrachlorophthalic anhydride
2.25 g	2-(tribromomethylsulfone)benzothiazole [AF-1]

The topcoat solutions were coated over the silver layer at a dry weight of 3.0 g/m². The layer was dried at 165°F (74°C) for four minutes.

The coated materials were then exposed with a laser sensitometer incorporating a 780 nm diode. After exposure,

the film strips were processed at 260°F (127°C) for ten seconds. The images obtained were evaluated by a densitometer. Sensitometric results include Dmin, Dmax, Spd (relative speed at a density of 1.0 above Dmin versus a control with no added isocyanate set at 100) and average contrast (Cont, measured from a density of 0.25 to 2.0 above Dmin). Sensitometry was also evaluated after shelf aging at room temperature and under accelerated aging conditions (120°F (49°C) and 50% RH). The results are listed in Table 2 and show the strong antifoggant effect of the isocyanates on shelf aging and accelerated aging.

TABLE 2

Ex	Grams IC per 40g Ag	Initial Sensitometry				7 Days at 120°F(49°C)/50%RH				2 Months Shelf Aging			
		Dmin	Dmax	Spd	Cont	Dmin	Dmax	Spd	Cont	Dmin	Dmax	Spd	Cont
A	none	0.14	3.17	100	4.34	0.34	3.37	46	3.28	0.35	3.29	93	3.69
1	0.020 IC-1	0.13	3.31	89	4.27	0.19	3.40	40	3.58	0.23	3.39	81	3.66
2	0.040 IC-1	0.12	3.37	79	4.28	0.15	3.44	35	3.30	0.19	3.41	71	3.63
3	0.080 IC-1	0.11	3.29	72	4.15	0.14	3.36	33	3.33	0.18	3.38	66	3.55
4	0.020 IC-2	0.13	3.29	81	4.15	0.16	3.42	40	3.39	0.20	3.34	76	3.77
5	0.041 IC-2	0.12	3.33	87	4.18	0.14	3.34	39	3.52	0.20	3.34	76	3.78
6	0.082 IC-2	0.12	3.22	81	4.22	0.13	3.37	36	3.36	0.17	3.30	66	3.77
7	0.009 IC-3	0.14	3.21	81	4.23	0.27	3.35	44	3.39	0.28	3.33	93	3.32
8	0.018 IC-3	0.14	3.19	95	4.18	0.27	3.38	42	2.92	0.28	3.27	83	3.53
9	0.036 IC-3	0.14	3.22	85	4.13	0.25	3.35	39	2.98	0.26	3.35	72	3.38
10	0.013 IC-4	0.14	3.29	95	4.40	0.31	3.43	46	3.11	0.31	3.32	89	3.54
11	0.027 IC-4	0.14	3.31	91	4.26	0.30	3.38	43	3.17	0.28	3.44	87	3.38
12	0.054 IC-4	0.12	3.36	85	4.13	0.28	3.39	42	3.15	0.25	3.43	77	3.24
13	0.014 IC-5	0.14	3.31	89	4.13	0.30	3.40	44	3.16	0.27	3.41	83	3.43
14	0.028 IC-5	0.13	3.37	85	4.21	0.30	3.44	41	2.81	0.29	3.45	81	3.63

15	0.056 IC-5	0.12	3.37	95	3.99	0.23	3.36	36	2.73	0.22	3.40	71	3.34
16	0.014 IC-6	0.15	3.28	95	4.08	0.23	3.46	44	3.25	0.30	3.40	89	3.44
17	0.028 IC-6	0.13	3.27	93	4.25	0.21	3.43	46	3.30	0.26	3.36	91	3.59
18	0.056 IC-6	0.14	3.20	93	4.08	0.18	3.36	41	3.11	0.22	3.31	79	3.53
19	0.014 IC-7	0.12	3.19	87	4.34	0.32	3.43	45	3.08	0.32	3.49	83	3.28
20	0.028 IC-7	0.13	3.29	91	4.04	0.31	3.47	43	3.16	0.31	3.42	87	3.40
21	0.056 IC-7	0.11	3.33	79	4.22	0.28	3.46	40	2.86	0.26	3.43	81	3.48
22	0.024 IC-8	0.15	3.28	98	4.07	0.28	3.58	44	2.95	0.33	3.43	91	3.70
23	0.049 IC-8	0.13	3.27	93	4.24	0.26	3.46	40	2.93	0.32	3.45	87	3.55
24	0.098 IC-8	0.14	3.23	87	4.01	0.19	3.41	35	2.77	0.24	3.30	77	3.38
25	0.031 IC-9	0.15	3.08	102	4.03	0.20	3.31	41	3.53	0.21	3.28	83	3.74
26	0.062 IC-9	0.17	3.17	95	3.86	0.16	3.33	43	3.60	0.20	3.30	76	3.78
27	0.124 IC-9	0.16	2.96	98	4.06	0.20	3.30	48	3.75	0.18	3.25	77	3.60

Example 28

An experiment was run to compare the effect of adding the isocyanate to the protective topcoat versus to the silver layer. The formulas were the same as described for examples 1-27. Example 2 and example 28 in Table 3 both contained 0.006 moles of IC-1 per one mole of total silver. The results are listed in Table 3 and show that the isocyanates act as strong antifoggants whether added to the silver or topcoat formulas.

TABLE 3

Isocyanate			Initial Sensitometry						7 Days at 120°F(49°C)/50%RH						2 Months Shelf Aging					
Ex	IC	Layer	Dmin	Dmax	Spd	Cont	Dmin	Dmax	Spd	Cont	Dmin	Dmax	Spd	Cont	Dmin	Dmax	Spd	Cont		
A	none	-	0.14	3.20	100	4.42	0.40	3.46	49	3.19	0.42	3.42	93	3.24						
2	IC-1	Silver	0.13	3.41	93	4.39	0.23	3.49	42	3.64	0.24	3.50	76	3.59						
28	IC-1	Topcoat	0.14	3.26	98	4.23	0.24	3.39	46	3.44	0.25	3.44	79	3.52						

Examples 29-32

The additive effect of the isocyanate, IC-1, on different antifoggants (AF-1 to AF-4) were evaluated in the following examples. The position of AF-1 in either the silver or topcoat formula was also tested. These examples were run with the IR formula described for examples 1-27 except with the changes listed in Table 4. The quantity of IC-1 was 0.006 moles per mole of silver when it was added to the coatings in Table 4. The results show improved fog control on shelf aging and accelerated aging when a combination of antifoggant (AF-1 to AF-4) and isocyanate are used.

TABLE 4

EX	Antifoggant (AF)		Moles AF per mole Silver ($\times 10^{-3}$)	IC-1	Initial Sensitometry			
	AF	Layer			Dmin	Dmax	Spd	Cont
B	AF-1	Silver	27.6	No	0.14	3.16	72	4.19
29	AF-1	Silver	27.6	Yes	0.13	3.25	66	4.39
A	AF-1	Topcoat	27.6	No	0.13	3.29	100	4.55
2	AF-1	Topcoat	27.6	Yes	0.12	3.39	98	4.39
C	AF-2	Topcoat	6.2	No	0.13	3.38	98	4.81
30	AF-2	Topcoat	6.2	Yes	0.12	3.47	83	4.69
D	AF-3	Topcoat	5.8	No	0.12	3.27	105	4.68
31	AF-3	Topcoat	5.8	Yes	0.11	3.37	100	4.50
E	AF-4	Topcoat	7.5	No	0.13	3.26	100	4.47
32	AF-4	Topcoat	7.5	Yes	0.12	3.40	91	4.51

TABLE 4 Con't

Ex	7 Days at 120°F(49°C)/50%RH					2 Months Shelf Aging				
	Dmin	Dmax	Spd	Cont		Dmin	Dmax	Spd	Cont	
B	0.16	3.21	46	3.49		0.17	3.18	62	3.86	
29	0.14	3.32	43	3.66		0.13	3.34	59	3.85	
A	0.19	3.49	57	3.54		0.18	3.34	98	3.84	
2	0.13	3.49	50	3.76		0.14	3.42	85	3.98	
C	2.48	-	-	-		0.16	3.41	63	4.18	
30	0.20*	3.51	28	3.71		0.13	3.50	54	4.11	
D	0.20	3.47	43	3.35		0.15	3.44	76	4.16	
31	0.12	3.36	35	3.87		0.12	3.44	66	4.04	
E	0.14	3.33	28	3.88		0.14	3.26	49	4.28	
32	0.12	3.36	22	3.88		0.11	3.39	42	4.23	

* heavy edge fog on strips

Example 33

The isocyanates were tested to determine whether the improved fog levels on aging was specific to the infrared or a more general effect. The silver and topcoat formulas were the same as those used in examples 1-27 except for the omission of the infrared dye, D-1, and the supersensitizer, MBI, and the addition of AF-1 to the silver layer and not the topcoat layer at 27.6×10^{-3} moles AF-1 per mole of silver. The two coatings (F and 33) in Table 5 were coated without any sensitizing dye.

The coated materials were exposed with an EG&G sensitometer at 10^{-3} seconds through a P-16 filter.

After exposure, the film strips were processed at 260°F (127°C) for ten seconds. Sensitometric results include Dmin, Dmax, Spd (speed at a density of 1.0), Ergs (speed or sensitivity at a density of 1.0) and Cont (contrast).

The results are compiled in Table 5 and show that the isocyanates reduce the fog increase on shelf aging for all systems, whether spectrally sensitized or not.

TABLE 5

Ex	Dye	Isocyanate		Initial Sensitometry						7 Days at 120°F(49°C)/50%RH			
		IC	Moles IC per mole Ag	Dmin	Dmax	Spd	Erge	Cont	Dmin	Dmax	Spd	Erge	Cont
F	none	none	-	0.09	3.50	2.04	92	8.07	0.19	3.80	2.30	51	5.54
33	none	IC-1	6×10^{-3}	0.09	3.62	2.05	89	8.43	0.12	3.99	2.22	60	6.06

2 Months Shelf Aging					
Ex	Dmin	Dmax	Spd	Erge	Cont
F	0.16	3.63	2.26	55	6.70
33	0.13	3.69	2.22	60	7.17

Examples 34-41

A green sensitized color photothermographic formula was tested to decide if isocyanates could again reduce the

fog increase on shelf aging.

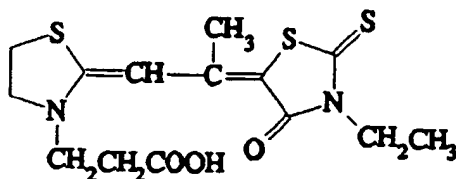
A silver halide-silver behenate dry soap was prepared by the procedures described in U.S. Pat. No. 3,839,049. The silver halide totalled 9% of the total silver while silver behenate comprised 91% of the total silver. The silver halide was a 0.055 μm silver bromiodide emulsion with 2% iodide.

A photothermographic emulsion was prepared by homogenizing 300 g of the silver halide-silver behenate dry soap described above with 525 g toluene, 1666 g 2-butanone and 9.0 g poly(vinylbutyral) (B-76, Monsanto).

The homogenized photothermographic emulsion (73 g) and 14.6 g 2-butanone were cooled to 55°F (13°C) with stirring. The following were added while the temperature was maintained at 55°F (13°C).

Ingredient	Mix
11.7 g poly(vinylbutyral) (B-76)	25 min
0.02 g PHP	1 hour
0.02 g PHP	1 hour
0.02 g PHP	4 hour
0.39 g CaBr_2 solution (10% w/v in MeOH) hold overnight at 55°F	0.5 hour

The silver photothermographic emulsion was completed on the second day by warming to 70°F (21°C) and then adding 5 g of green sensitizing dye solution (0.0013 g D-2 dye and 5 g MeOH).



D-2

A premix (100 g) was also prepared by combining the chemicals listed below:

0.97 g	ethyl ketazine
1.89 g	phthalazinone
0.24 g	AF-1
85.80 g	tetrahydrofuran
6.76 g	polyvinyl(chloride-acetate-alcohol) tripolymer (VAGH, Union Carbide)
4.34 g	poly(vinylbutyral) (B-76, Monsanto)

A mixture was prepared by combining 6 grams of the silver formulation with 13.5 grams of premix. The photothermographic mixture was coated on 3 mil ($0.76 \times 10^{-4}\text{m}$) opaque polyester film filled with barium sulfate and dried at 170°F (77°C) for four minutes. The dry coating weight was 5 g/m².

An active, protective topcoat solution (100 g) was prepared with the following ingredients:

53.56 g	acetone
26.44 g	2-butanone
10.68 g	toluene
8.65 g	polystyrene(Styrone 685D, Dow)
0.67 g	(Solvent or isocyanate test compound)

The topcoat solutions were coated over the silver layer at a dry weight of 3.5 g/m². The topcoat was dried at 170°F (77°C) for four minutes. For comparison, 0.11 moles of IC-1 were added per mole of silver in example 34.

The coated materials were exposed for 10^{-3} seconds with a xenon flash from an EG&G sensitometer. The flash exposure was filtered with a green, Wratten 58 filter which has a maximum output at 530 nm. The film strips were then

EP 0 600 586 B1

processed at 277°F (136°C) for 8 seconds to generate a magenta colored image. Sensitometric results include Dmin, Dmax, Spd (speed at a density of 0.6 above fog), Ergs (speed or sensitivity at a density of 0.6 above fog) and Cont (average contrast).

The results are compiled in Table 6 and show that the isocyanates reduce the fog increase for a color photothermographic system.

5

10

15

20

25

30

35

40

45

50

55

TABLE 6

Ex	IC	Grams IC per 100g Topcoat	Initial Sensitometry					3 Month Shelf Aging				
			Dmin	Dmax	Spd	Erge	Cont	Dmin	Dmax	Spd	Erge	Cont
C	none	0	0.13	2.27	2.03	93	4.61	0.79	2.35	1.79	162	1.49
34	IC-1	0.67	0.12	2.31	1.93	117	4.44	0.61	2.38	1.82	151	2.56
35	IC-2	0.67	0.12	2.37	1.94	115	4.80	0.53	2.40	1.86	138	2.52
36	IC-3	0.67	0.10	1.82	1.56	275	2.68	0.17	1.85	1.38	423	1.90
37	IC-4	0.67	0.10	2.15	1.75	178	2.50	0.26	2.22	1.54	288	2.47
38	IC-5	0.67	0.11	2.29	1.77	170	2.83	0.24	2.31	1.58	263	2.52
39	IC-6	0.67	0.13	2.24	1.94	115	4.12	0.40	2.44	1.85	141	3.21
40	IC-7	0.67	0.10	2.23	1.76	174	2.80	0.31	2.25	1.52	302	2.31
41	IC-8	0.67	0.12	2.27	1.95	112	4.27	0.41	2.41	1.78	166	2.76

TABLE 6 Con't

24 Hours at 120°F(49°C)/50%RH					
Ex	Dmin	Dmax	Spd	ErgB	Cont
G	0.23	2.24	1.85	141	2.59
34	0.13	2.36	1.76	170	2.50
35	0.16	2.39	1.86	138	3.59
36	0.11	1.42	1.22	602	1.40
37	0.11	2.07	1.55	282	2.00
38	0.14	2.10	1.46	347	2.17
39	0.14	2.36	1.79	162	3.02
40	0.11	2.06	1.54	288	2.01
41	0.16	2.36	1.75	178	3.09

Examples 42 and 43

A further improvement on the present invention is to combine the antifoggant (AF-1 to AF-4) and isocyanate with compounds covered in EP-A-0600589. The formula was the same as presented in Examples 34-41 except that the preformed silver halide was 0.075 μm and 100% bromide. Example 43 contained isocyanate (IC-2) and also 0.135 g of vinyl sulfone, VS, in 100 grams of topcoat. Table 7 shows that the best fog stability under accelerated aging conditions for the green sensitized, color photothermographic formula was obtained with a combination of isocyanate and vinyl sulfone (VS).

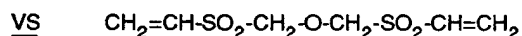
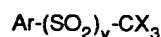


TABLE 7

Ex	Added to 100g Topcoat		Initial Sensitometry					7 Days at 120°F/50% RH				
	IC-2	VS	Dmin	Dmax	Spd	Ergs	Cont	Dmin	Dmax	Spd	Ergs	Cont
H	none	none	0.13	2.22	2.43	37	3.83	0.32	2.23	2.51	31	1.77
42	0.67 g	none	0.12	2.31	2.44	36	2.37	0.25	2.38	2.19	64	2.15
43	0.67 g	0.135 g	0.12	2.36	2.40	40	3.43	0.17	2.47	2.62	24	1.58

Claims

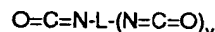
1. A photothermographic emulsion comprising in one or two layers a silver salt of an organic acid, silver halide, a reducing agent for silver ion, and a binder, the silver salt of an organic acid and the silver halide being present in one layer, characterised in that the emulsion contains, as an antifoggant, the combination of 1) at least one compound having an isocyanate group, and 2) a halogenated antifoggant compound which has an aromatic or heteroaromatic group having at least one perhalogenated alkyl group thereon.
2. An emulsion as claimed in Claim 1 in which the halogenated antifoggant compound has a brominated alkyl group thereon.
3. An emulsion as claimed in Claim 2 in which the halogenated antifoggant compound has at least one tribromomethane group thereon.
4. An emulsion as claimed in Claim 3 in which the tribromomethane group is directly attached to an aromatic or heteroaromatic group or the tribromomethane group is bonded to an aromatic or heteroaromatic group through a linking group.
5. An emulsion as claimed in Claim 4 in which said linking group is sulfonyl.
6. An emulsion as claimed in any preceding Claim in which the halogenated antifoggant compound has the formula:



in which:

Ar is an aromatic or heteroaromatic group, and
y is 0 or 1.

7. An emulsion as claimed in any preceding Claim in which the compound having an isocyanate group is represented by the formula



wherein

v is 0, 1, or 2, and

L is a linking group or when v is 0, L is a terminating group.

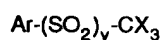
8. An emulsion as claimed in Claim 7 in which L is selected from alkyl, alkene, aryl, and mixed alkylaryl groups.
9. An emulsion as claimed in any preceding Claim in which the compound having an isocyanate group is present in an amount in the range 0.002 to 2 moles per mole of silver.
10. An emulsion as claimed in any preceding Claim in which the halogenated antifoggant compound is present in an amount in the range 5×10^{-4} to 0.5 mole per mole of silver.

Patentansprüche

1. Photographische Emulsion, umfassend in einer oder zwei Schichten ein Silbersalz einer organischen Säure, Silberhalogenid, ein Reduktionsmittel für Silberionen und ein Bindemittel, wobei das Silbersalz einer organischen Säure und das Silberhalogenid in einer Schicht vorhanden sind, dadurch gekennzeichnet, daß die Emulsion als Antischleiermittel eine Kombination von 1) mindestens einer Verbindung mit einem Isocyanatrest und 2) einer halogenierten Antischleiermittelverbindung enthält, die einen aromatischen oder heteroaromatischen Rest mit min-

destens einem perhalogenierten Alkylrest aufweist.

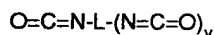
2. Emulsion nach Anspruch 1, wobei die halogenierte Antischleiermittelverbindung einen bromierten Alkylrest aufweist.
3. Emulsion nach Anspruch 2, wobei die halogenierte Antischleiermittelverbindung mindestens eine Tribrommethangruppe aufweist.
4. Emulsion nach Anspruch 3, wobei die Tribrommethangruppe direkt an einen aromatischen oder heteroaromatischen Rest gebunden ist oder die Tribrommethangruppe über einen verbindenden Rest an einen aromatischen oder heteroaromatischen Rest gebunden ist.
5. Emulsion nach Anspruch 4, wobei der verbindende Rest eine Sulfonylgruppe ist.
6. Emulsion nach einem der vorstehenden Ansprüche, wobei die halogenierte Antischleiermittelverbindung die Formel



hat, worin:

Ar ein aromatischer oder heteroaromatischer Rest und
y 0 oder 1 ist.

7. Emulsion nach einem der vorstehenden Ansprüche, wobei die Verbindung mit einem Isocyanatrest die Formel



hat, worin

v 0, 1 oder 2 ist, und
L ein verbindender Rest ist, oder
wenn v 0 ist, L ein endständiger Rest ist.

8. Emulsion nach Anspruch 7, wobei L gewählt ist aus einem Alkyl-, Alken-, Aryl- und einem gemischten Arylrest.
9. Emulsion nach einem der vorstehenden Ansprüche, wobei die Verbindung mit einem Isocyanatrest in einer Menge im Bereich von 0,002 bis 2 Mol pro Mol Silber vorliegt.
10. Emulsion nach einem der vorstehenden Ansprüche, wobei die halogenierte Antischleiermittelverbindung in einer Menge im Bereich von 5×10^{-4} bis 0.5 Mol pro Mol Silber vorliegt.

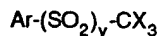
Revendications

1. Emulsion photothermographique comprenant, dans une ou deux couches, un sel d'argent d'un acide organique, un halogénure d'argent, un agent réducteur de l'ion argent, et un liant, le sel d'argent d'un acide organique et l'halogénure d'argent étant présents dans une couche, caractérisée en ce que l'émulsion contient, en tant qu'antivoile, la combinaison

- 1) d'au moins un composé ayant un groupe isocyanate, et
- 2) d'un composé antivoile halogéné, ayant un groupe aromatique ou hétéroaromatique portant au moins un groupe alkyle perhalogéné.

2. Emulsion selon la revendication 1, dans laquelle le composé antivoile halogéné porte un groupe alkyle bromé.

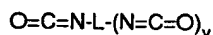
3. Emulsion selon la revendication 2, dans laquelle le composé antivoile halogéné porte au moins un groupe tribromométhane.
4. Emulsion selon la revendication 3, dans laquelle le groupe tribromométhane est directement fixé à un groupe aromatique ou hétéroaromatique, ou encore le groupe trifluorométhane est lié à un groupe aromatique ou hétéroaromatique par l'intermédiaire d'un groupe de liaison.
5. Emulsion selon la revendication 4, dans laquelle ledit groupe de liaison est le groupe sulfonyle.
6. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle le composé antivoile halogéné a la formule



dans laquelle :

Ar est un groupe aromatique ou hétéroaromatique, et
y vaut 0 ou 1.

7. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle le composé ayant un groupe isocyanate est représenté par la formule



dans laquelle

v vaut 0, 1 ou 2, et

L est un groupe de liaison, ou encore, quand v vaut 0, L est un groupe terminal.

8. Emulsion selon la revendication 7, dans laquelle L est choisi parmi l'ensemble comprenant les groupes alkyle, alcène, aryle, et alkyle-aryle mélangés.
9. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle le composé ayant un groupe isocyanate est présent en une quantité comprise dans l'intervalle de 0,002 à 2 moles par mole d'argent.
10. Emulsion selon l'une quelconque des revendications précédentes, dans laquelle le composé antivoile halogéné est présent en une quantité comprise dans l'intervalle de $5 \cdot 10^{-4}$ à 0,5 mole par mole d'argent.